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SPECIFICS OF ELECTRICAL CONDUCTION IN ALKALI-SILICATE GLASSES

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A substantial amount of experimental data on electric conduction in alkaline-silicate glasses with a different content of alkaline oxide published by various authors is analyzed. It is established that for nonliquating glasses the dependence of the conductivity on the alkaline oxide content is best expressed via its dependence on the mean distance between the alkaline cations.

Electrical conduction in alkali-silicate glasses is purely ionic, and the cation of an alkaline metal is an electric charge carrier [1, 2]. Therefore, one might expect a proportional dependence of electrical conductivity on the concentration of the alkaline oxide R_2O . However, when the content of the alkaline oxide increases 5 times, the conductivity grows by about 5 orders of magnitude [3, 4], and the authors in [2 – 4] attribute this phenomenon to the heterogeneity of the chemical composition of the medium in which the cation migrates.

Glasses contain areas with an increased content of R_2O (polar zones [2]) in which the concentration of dissociated alkaline metal cations R^+ is substantial, and areas with a low content of R_2O (nonpolar zones) in which, accordingly, the concentration of dissociated ions is lower. Considering that only dissociated ions participate in electrical conduction, the conductivity depends on the mutual arrangement of the polar and nonpolar areas. If the polar groups are associated and form closed inclusions, the conductivity is determined by the low quantity of dissociated cations in the single-bond nonpolar medium. In the case of a high concentration of R_2O , the polar microgroups aggregate in a continuous zone, increasing the conductivity of the glass due to the increased concentration of dissociated ions in this zone. This is an interpretation proposed to account for the specifics of the conduction of lithium and sodium silicate glasses, in contrast to potassium-silicate glass, which has a more homogeneous composition [4].

The alkali-silicate glasses that are not prone to liquation (potassium, rubidium, and cesium) and, therefore, are regarded as homogeneous do not exhibit a jump in their conductivity depending on the composition. However, the increase in the conductivity of these glasses with increasing concentration of the alkaline oxide significantly exceeds the

proportional dependence between these magnitudes and in this case cannot be accounted for by the competition between heterogeneous zones with different conductivities. Hence it follows that the number of carriers is influenced not only by the concentration of the alkaline metal ions but also by the interaction between these ions depending on the distance between the cations. The mechanism of such interaction is well studied for the process of impurity electron conduction in noncrystalline materials [5]. In particular, due to the reactions between the impurity centers, the following factor appears in the dependence of electrical conductance on the impurity content:

$$\exp(-2\lambda L), \quad (1)$$

where λ is a constant depending on the energy parameters of the reacting centers and the type of charged particle; L is the mean distance between the impurity centers.

Assuming that the reaction between the neighboring ions of an alkaline metal is described by an expression containing a factor of form (1), we can construct the dependence of the logarithm of the conductivity of glasses σ on the mean distance between the cations L :

$$L = \sqrt[3]{\frac{M_B}{\rho N_0 c_{eq}}},$$

where M_B is the molar weight of the glass; ρ is the glass density; N_0 is Avogadro's constant; c_{eq} is the molar concentration of the alkaline oxide.

The needed data for different glass compositions are taken from a reference book [6]. Considering the expected spread in data, preference was given to data supplied by the authors who have performed integrated studies of the glass compositions that are of interest to us. The electric properties

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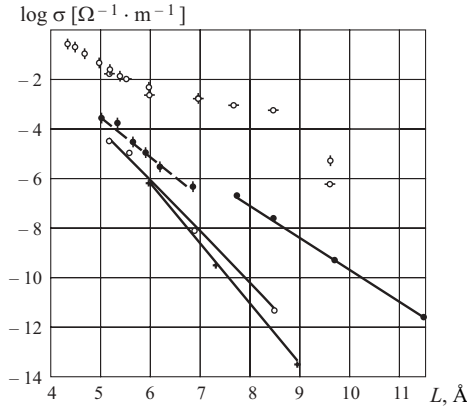


Fig. 1. Dependence of the conductivity σ of alkaline-silicate glasses on the mean distance between cations L : \diamond) $\text{Na}_2\text{O} - \text{SiO}_2$, 300°C (O. A. Mazurin [7]); \odot) $\text{Na}_2\text{O} - \text{SiO}_2$, 300°C (K. F. Evstrop'ev [6]); \bullet) $\text{K}_2\text{O} - \text{SiO}_2$, 150°C (O. A. Mazurin [6]); \bullet) $\text{K}_2\text{O} - \text{SiO}_2$, 150°C (K. F. Evstrop'ev [6]); \circ) $\text{Rb}_2\text{O} - \text{SiO}_2$, 100°C (R. Charles [6]); $+$) $\text{Cs}_2\text{O} - \text{SiO}_2$, 100°C (R. Charles [6]).

of sodium- and potassium-silicate glasses at temperatures of 150 and 300°C are based on the data obtained by O. A. Mazurin et al. and K. F. Evstrop'ev's team [6], and the data on rubidium and cesium silicates are taken from the study by R. Charles [6]. The data for sodium-silicate glasses are presented for reference purposes and clearly demonstrate a difference depending on the type of distribution of the modifier ions in sodium-silicate glasses, on the one hand, and in potassium-, rubidium-, and cesium-silicate glasses, on the other hand.

It can be seen in Fig. 1 that the dependence of conductivity on L in glasses with K, Rb, and Cs oxides is well approximated by the expression

$$\sigma = \sigma_L e^{-\alpha L} \quad (2)$$

within the whole range of compositions, whereas in sodium-silicate glass the range of compositions is split in two segments, in one of which dependence (2) is satisfied, and in the other one it is not.

The concentration dependence of type (2) is maintained at all temperatures under which the measurements were conducted. It is only the factor σ_L and the parameter α that vary depending on the modifier type and the temperature.

Since electric conduction is an activation process, its temperature dependence σ is usually represented in the following form:

$$\sigma = \sigma_0 e^{-E/RT},$$

where E is the activation energy, which depends on the type of cation and its concentration in the glass, and taking into account expression (2), its dependence on L should be linear:

$$E = E_0 + \beta L. \quad (3)$$

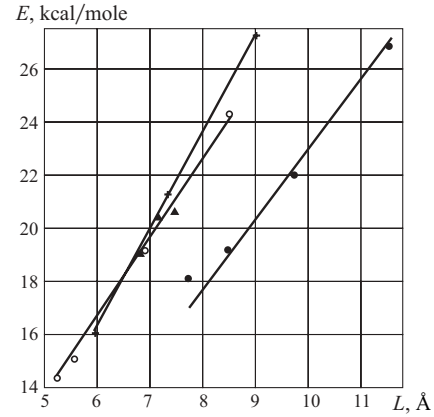


Fig. 2. Dependence of the conductance activation energy E in alkaline-silicate glasses on the mean distance between cations L : \bullet) $\text{K}_2\text{O} - \text{SiO}_2$ (K. F. Evstrop'ev [6]); \circ) $\text{Rb}_2\text{O} - \text{SiO}_2$ (R. Charles [6]); $+$) $\text{Cs}_2\text{O} - \text{SiO}_2$ (R. Charles [6]); \blacktriangle) $\text{Cs}_2\text{O} - \text{SiO}_2$ (R. Terai [6]).

The data in Fig. 2 corroborated this assumption. The values of activation energy for rubidium and cesium silicates shown in Fig. 2, are taken from the above authors, whereas the values for potassium-silicate glasses are the estimated values calculated on the basis of the data on electrical conductivity at temperatures of 150 and 300°C [6]. Consequently, all further calculations for potassium-silicate glasses relate only to this group of data.

The results of approximation of E depending on L using expression (3) for silicate glasses with different modifiers are represented in Table 1. Correlating expressions (2) and (3), one can write

$$\alpha = \gamma + \frac{\beta}{RT};$$

$$\sigma = \sigma_L \exp(-\gamma L) \exp\left(-\frac{\beta L}{RT}\right) = \sigma_0 \exp\left(-\frac{E_0}{RT}\right) \exp\left(-\frac{\beta L}{RT}\right),$$

whence

$$\sigma_L \exp(-\gamma L) = \sigma_0 \exp\left(-\frac{E_0}{RT}\right),$$

where σ_L does not depend on L , and σ_0 does not depend on T .

TABLE 1

Glass	E_0 , kcal/mole	$\beta \times 10^{10}$, kcal/(mole · m)	$\gamma \times 10^{10}$, m ⁻¹	log A [$\Omega^{-1} \cdot \text{m}^{-1}$]
$\text{K}_2\text{O} - \text{SiO}_2$	-3.53	2.65	0	2.00
$\text{Rb}_2\text{O} - \text{SiO}_2$	-1.65	3.03	0.77	5.56
$\text{Cs}_2\text{O} - \text{SiO}_2$	-5.80	3.70	0.50	4.46

Therefore $\sigma_0 e^{\gamma L} = \sigma_L e^{-E_0/RT} = A$ and depends neither on T nor on L , and one can write

$$\sigma = A e^{-\gamma L - E/RT}, \quad (4)$$

or

$$\log \sigma = \log A - \frac{\gamma L + E/RT}{2.3}.$$

In this case E is determined using expression (3) and all values needed for a calculation are given in Table 1.

Expression (4) contains terms reflecting different forms of dependence of conductivity on the mean distance between cations. One form of dependence arises due to the effect of the cation concentration on the process activation energy $e^{-E/RT}$. Another appears to be a contribution of the tunnel mechanism to the probability of dissociation of cations $e^{-\gamma L}$.

Compare expression (4) with the generally accepted equation for ionic conduction [8]

$$\sigma = \frac{e^2 a^2 N v}{kT} p e^{-E/RT},$$

where e is the electron charge; a is the distance between the neighboring interstices; N is the number of cations per volume unit.

Then for potassium-silicate glass ($\gamma = 0$) we find that the factor p determining the share of ions capable of migration [8] coincides with the factor $e^{-\gamma L}$:

$$A = \frac{e^2 a^2 N v}{kT} = \sigma_0.$$

The mean distance between the neighboring oxygen atoms in these glasses varies within the limits of 3.5 – 4.0 Å depending on the composition. The distance between the neighboring interstices through which a cation can migrate can be estimated as the distance between the centers of the adjacent faces of the tetrahedron, which is of the order of 1.5 Å.

Taking $a = 1.5 \text{ Å}$, $v = 10^{12} \text{ sec}^{-1}$, and $T = 573 \text{ K}$, for a potassium-silicate glass containing 7.5 mol.% potassium oxide we obtain $\log A = \log \sigma_0 = 2.06 \Omega^{-1} \cdot \text{m}^{-1}$.

In other glasses ($\gamma \neq 0$), σ_0 depends on L and

$$\log \sigma_0 = \log A - \frac{\gamma L}{2.3}.$$

It is established that the dependence of conductance in nonliquating alkaline glasses on the content of alkaline oxide is best expressed via its dependence on the mean distance between the alkaline cations. This dependence is a product of two exponential factors: one of them coincides with the factor present in the expression constructed for the jumping electron conduction, and in the second one, which is the activation factor, activation energy is linearly related to the mean distance between the alkaline cations.

Thus, the expression $\sigma = A e^{-\gamma L - E/RT}$ can be used for approximate computations of conductivity in potassium, rubidium, and cesium silicate glasses.

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